



**DURABILITY OF FIBRE REINFORCED POLYMER (FRP)
COMPOSITES FOR CONSTRUCTION**

***DURABILITÉ DES COMPOSITES EN POLYMÈRES
RENFORCÉS DE FIBRES (PRF) POUR LA CONSTRUCTION***

ENVIRONMENTAL EFFECTS ON COMPOSITE MATRIX RESINS USED IN CONSTRUCTION

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ABSTRACT

One of the obstacles hindering the acceptance of polymer composites in civil engineering applications is the susceptibility of the polymeric matrix to degradation initiated by moisture, temperature, and corrosive chemical environments. The objective of this study was to characterize chemical and physical changes in polymeric matrix resins following exposure to these environments. Resin systems studied were vinyl ester and isophthalic polyester, both of which are suitable for use in construction applications. Unreinforced free films were exposed to water, alkaline and saline environments at ambient and elevated temperatures for extended periods of time. Changes in strength and thermophysical properties were evaluated through tensile testing, dynamic mechanical thermal analysis (DMTA) and thermogravimetric analysis (TGA). Chemical degradation of the polymers was characterized using Fourier transform infrared (FTIR) spectroscopy. Energy dispersive x-ray (EDX) analysis of specimens following exposure was carried out to determine if ion diffusion into the bulk polymer occurred. Changes in the glass transition temperatures and tensile strengths of the polymers were observed after prolonged exposure at elevated temperature, particularly in the case of the isophthalic polyester. Examination of the polymers following immersion in salt water and alkaline solution showed essentially no ionic penetration into the bulk. Spectroscopic analysis of chemical structure prior to and following exposure revealed varying degrees of ester hydrolysis.

**Durability of Fibre Reinforced Polymer (FRP) Composites
for Construction (CDCC'98), 1st International
Conference. Proceedings. 1998, Canada, Benmokrane, B.,
Rahman, H., Editors, 229-241 pp, 1998.**

INTRODUCTION

At the present time, deterioration of the world's infrastructure is motivating the use of advanced materials, such as fiber-reinforced polymer composites, in civil engineering applications. These materials, due to their high specific strength, light weight, fatigue and corrosion resistance, have become attractive candidates for use in primary structures as well as in rehabilitation and retrofitting of existing structures.

Although it is one of the key constituents of a fiber-reinforced polymer composite, the polymer matrix is often considered to be the weak link in the system. Polymer composites in outdoor applications are susceptible to photo-initiated oxidation (Halliwell, 1992) and are also known to be sensitive to moisture-induced damage (French and Pritchard, 1992), alkaline environments and saline conditions (Sonawala and Spontak, 1996). It is necessary to understand the mechanisms which govern polymer degradation, not only to optimize material performance, but to provide information which can be used in accelerated aging tests.

The objective of this study was to systematically study chemical and physical changes in polymer matrix composites following exposure to moisture, alkaline and saline conditions at ambient and elevated temperatures. Measurement of physicochemical properties can yield critical information on mechanisms of degradation and can be used to model mechanical performance. Data obtained at elevated temperature are important in determining the validity of accelerated aging tests utilizing temperature as the accelerating factor. The long term goal is to identify factors which contribute to matrix resin degradation under environmental and mechanical stresses, and to determine if the mechanisms of degradation are altered by elevated temperature.

EXPERIMENTAL

Specimen Preparation

Commercial vinyl ester and isophthalic polyester (isopolyester) resins were selected for this study. Vinyl ester specimens were prepared by hand-mixing the resin, 3% by mass of a methyl ethyl ketone peroxide (MEKP) catalyst and a small amount (less than 0.5% by mass) of a silicone defoaming agent until thoroughly blended. A similar procedure was followed for the isopolyester specimens, except that only 2% by mass of the MEKP catalyst and no silicone defoamer were used. Because both the vinyl ester and isopolyester resins were already formulated with accelerator and promoter, only the addition of the catalyst was necessary to initiate crosslinking.

Free films were produced by molding between two acrylic plates to prevent oxygen inhibition of the curing process. Poly(ethylene terephthalate) sheets served as release films and spacers for obtaining desired film thickness. Films were allowed to gel at room temperature, followed by a 2 h/150 °C postcure. Final film thicknesses ranged from 230 μm to 260 μm .

Dogbone-shaped tensile specimens were produced for mechanical testing in a custom-designed mechanical testing device. The procedure for making dogbones is similar

to that described above for films, except that a 1.5 mm thick poly(tetrafluoroethylene) dogbone mold was used. The gage section of the dogbone specimens was 4 mm wide and 25 mm long, with thicknesses ranging from 1.3 mm to 1.5 mm.

Exposure Environments

Free films (50 mm x 50 mm) and dogbone specimens were immersed in distilled water, salt water (to simulate a marine or offshore environment) and an artificial concrete pore solution (to simulate the alkaline environment of a cementitious material, as would be encountered by reinforcing bars) for 1300 hours at ambient temperature. Salt water solution was composed of 0.58 mol/L NaCl in distilled water. Concrete pore solution was formulated according to the procedure of Christensen et al. (1992) and is composed of 0.32 mol/L KOH, 0.17 mol/L NaOH and 0.07 mol/L $\text{Ca}(\text{OH})_2$ in distilled water. This solution has a pH of approximately 13.5. Specimens were immersed in glass jars at ambient temperature (nominally 22 °C), 60 °C and 90 °C. Elevated temperature specimens were stored in a circulating air oven set at the appropriate temperature. After immersion, samples were dried for one week under vacuum at 35 °C prior to thermal, spectroscopic and tensile measurements.

Thermal Analysis

Dynamic Mechanical Thermal Analysis (DMTA): 12 mm x 35 mm films were tested in tensile mode in a Rheometrics Solids Analyzer (RSA) II* at a frequency of 10 Hz and 0.05% dynamic strain. Analysis was carried out from 30 °C to 180 °C, with data being recorded in 2 °C increments. Samples were pre-strained to maintain a constant state of tension throughout the experiment and to prevent film buckling. Three samples of each polymer were analyzed for each exposure condition.

Thermogravimetric Analysis (TGA): Thermogravimetric analysis was carried out on a TA Instruments TGA 2950 at a heating rate of 5 °C per minute in a nitrogen atmosphere. Mass loss was characterized in the range from 25 °C to 400 °C. Typical sample size was 10 mg and 3 runs were carried out for each specimen. [*Note: Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by NIST, nor is it intended to imply that the materials or equipment identified are necessarily the best available for this purpose]

Fourier Transform Infrared (FTIR) Spectroscopy

Fourier transform infrared (FTIR) analysis was performed on a Nicolet Magna-IR 560 infrared spectrometer. Samples which had been dried under vacuum as described above were pulverized, mixed with dry, spectroscopic grade potassium bromide and pressed into pellets. Spectra were collected in a dry air atmosphere and ratioed to a blank background. One hundred scans were collected and averaged at a resolution of 4 cm^{-1} .

Tensile Testing

The custom-designed testing device used for determining tensile strengths of the dogbone specimens consisted of a screw-driven linear actuator equipped with a 227 kg (500 lb) load cell and linear voltage displacement transducer (LVDT). Dogbone specimens were secured in machined aluminum grips which conformed to the shape of the dogbone end tabs and loaded at the rate of 1 mm/s. Three to five samples were tested for each polymer and exposure condition. Tensile strengths of the exposed specimens is reported as normalized tensile strength with respect to the control specimens.

Energy Dispersive X-ray (EDX) Analysis

In order to determine if ions from the salt and pore solutions actually diffused into the resins, 25 mm diameter rods of vinyl ester and isopolyester were immersed in salt solution and pore solution at ambient temperature and 60 °C for 60 days. The rods were then scribed and fractured. Spots at the outermost edge of the sample as well as 200 μ m into the bulk were analyzed with an ISI SX-40 scanning electron microscope equipped with a Noran 5402 EDX detector. Analyzed areas were scanned for sodium, potassium and chlorine.

RESULTS AND DISCUSSION

Thermal Analysis

Figures 1 and 2 show comparisons of T_g s obtained by DMTA of the dried vinyl ester and isopolyester films as a function of immersion time. The glass transition temperature was taken to be the peak of the loss modulus (E'') curve. The standard deviation of the data was estimated from a set of 10 replicates to be 2 °C.

In the case of vinyl ester, only minor changes (2 °C to 3 °C) in the T_g are observed following exposure to any solution, at any temperature or time. This is an indication that the structure of the vinyl ester has not been significantly disrupted by any of the exposure environments. Increases in T_g were observed for isopolyester following exposure at water, salt water and pore solution at 60 °C and 90 °C. This can be explained by the loss of low molecular segments leading to embrittlement and subsequent increase in T_g (Apicella et al., 1983). Isopolyester specimens aged at 90 °C for 10 weeks were too severely degraded for DMTA analysis.

Mass loss measured by TGA up to 300 °C is charted in Figure 3. The standard deviation of this measurement was calculated from a set of 5 replicates to be 0.5%. The region up to 300 °C is considered to be strongly correlated to changes in molecular structure (Prian et al., 1997). Above 300 °C, mass loss is rapid and severe, and is no longer sensitive to previous environmental history. It can be seen in Figure 3(a) that the vinyl ester specimens show mass loss comparable to the control, with the exception of specimens exposed to 90 °C water, which have significantly higher mass loss. As shown in Figure

3(b), only isopolyester specimens exposed to 60 °C pore solution and 90 °C pore solution exhibit mass loss more severe than that of the control.

Tensile Testing

Normalized tensile strengths of vinyl ester and isopolyester specimens (reported as percentage of tensile strength retained relative to the control) as a function of immersion time are shown in Figures 4 and 5. Standard deviation of the reported data is calculated to be 23%. An overall decrease in tensile strength was observed over the exposure period for all environments and temperatures. Specimens exposed to elevated temperature pore solution exhibited the most severe degradation. In the case of isopolyester in 90 °C pore solution, specimens were so severely degraded after 10 weeks that they could no longer be tested. Degradation in strengths of isopolyester and vinyl ester composites exposed to alkaline environments was also reported by Altizer et al.(1996) and Sonawala and Spontak (1996).

Fourier Transform Infrared Spectroscopy

Relative to the control spectrum, very few changes were seen in the infrared spectra of vinyl ester specimens exposed to salt solution or pore solution. For all exposure conditions and temperatures, a small peak at 3740 cm^{-1} was seen following exposure, the identity of which is unknown. Vinyl ester exposed to 90 °C water exhibited the greatest degree of change in band intensity and position; recall that this exposure condition also resulted in the highest mass loss in the TGA analysis relative to the control.

A number of spectral changes were also observed for the isopolyester specimens. Figure 6 shows the spectrum of isopolyester following exposure to pore solution at ambient temperature, 60 °C and 90 °C. Significant changes are seen in the 60 °C and 90 °C spectra, which again correspond to the specimens which exhibited the greatest mass loss in the TGA analysis. Changes include a relative decrease in the intensity of the ester carbonyl peak at 1728 cm^{-1} and the appearance of the carboxylate doublet in the 1584 cm^{-1} to 1600 cm^{-1} region. The decrease in ester functionality paired with the appearance of carboxylate ion are consistent with ester hydrolysis, which yields carboxylic acid and hydroxyl by-products. In ionic solution, the carboxylic acid is then converted to the carboxylate salt. Nguyen and Byrd observed the carboxylate doublet for stearic acid in ionic solution (1996). Similar spectral changes were observed for isopolyester and vinyl ester materials by Ghorbel and Valentin (1993).

Energy Dispersive X-ray Analysis (EDX)

Appreciable amounts of sodium, potassium or calcium were found only in the interior of the isopolyester specimen exposed to 60 °C pore solution. However, this is attributed to the fact that this particular specimen was visibly degraded and ion transport most likely occurred through the damaged resin. Specimen with no visible surface degradation showed no ions in the bulk. It was shown by Katsuki and Uomoto (1995), using electron probe analysis that sodium ions penetrated into fiber-reinforced vinyl ester

rods following 60 days in 2 mol/L NaOH. On the other hand, Soulier reported that no transport of sodium or chloride ions occurred into fiber-reinforced epoxy composites immersed in salt solutions when analyzed by atomic absorption spectrometry (Soulier et al., 1988).

SUMMARY

Unreinforced free films of vinyl ester and isophthalic polyester were characterized with DMTA, DSC, TGA, FTIR and tensile testing following exposure to water, alkaline and saline environments at ambient and elevated temperatures for extended times. Only minor changes in the glass transition temperatures were observed, but changes in the tensile strengths of exposed specimens were appreciable, particularly in the case of the isophthalic polyester exposed to elevated temperature pore solution. Spectroscopic analysis of the resins following exposure revealed varying degrees of ester hydrolysis. Examination of the polymers with EDX following immersion in salt solution and simulated concrete pore solution showed essentially no ionic penetration into the bulk.

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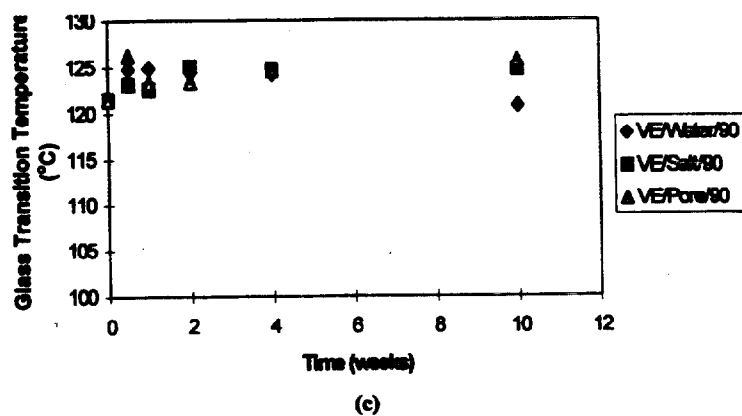
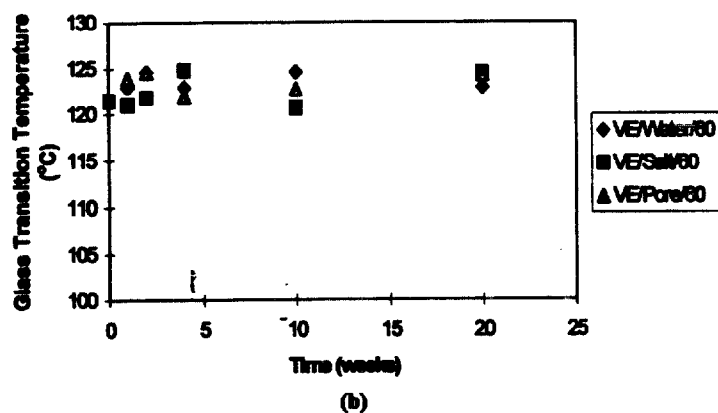
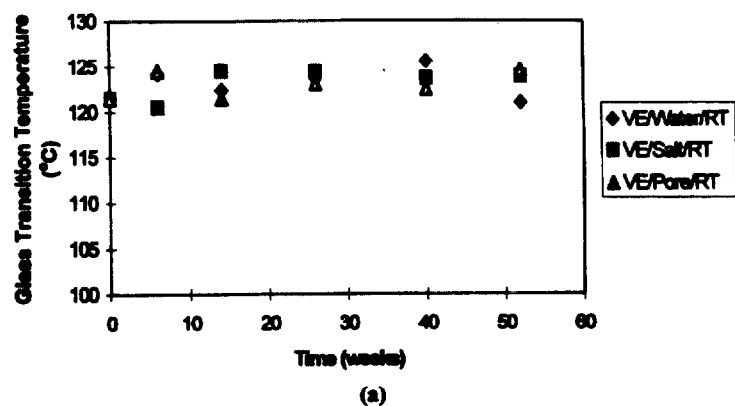
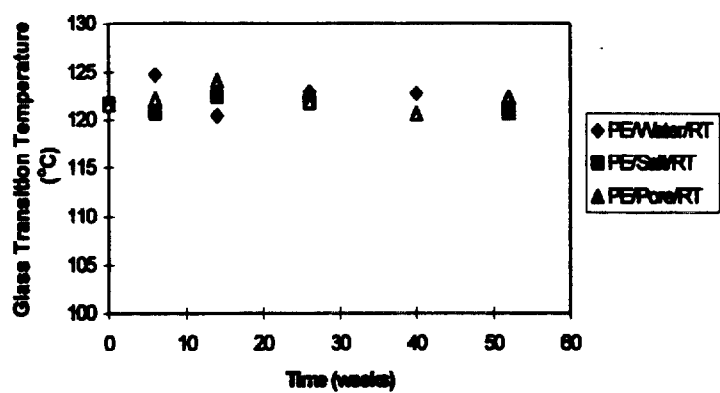
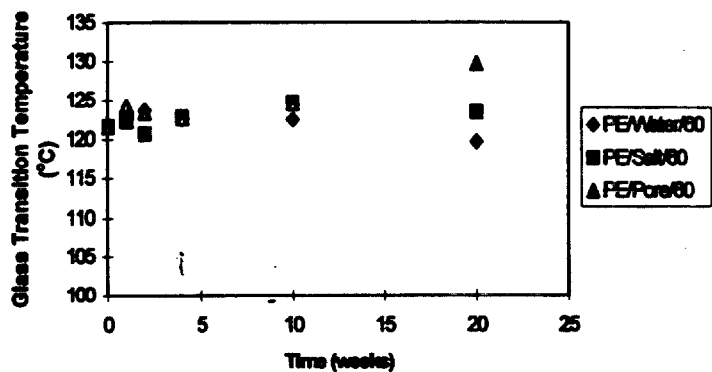


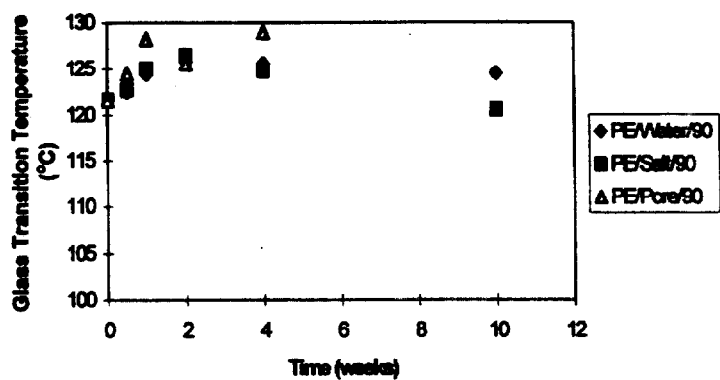
Figure 1: Vinyl ester glass transition temperatures determined by DMTA following exposure to water, salt solution and concrete pore solution at (a) ambient temperature, (b) 60 °C, and (c) 90 °C (estimated standard deviation is ± 2 °C).



(a)

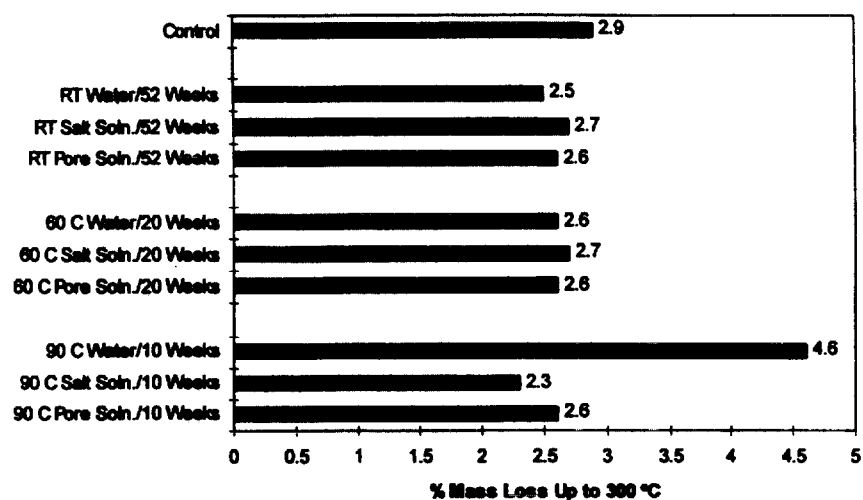


(b)

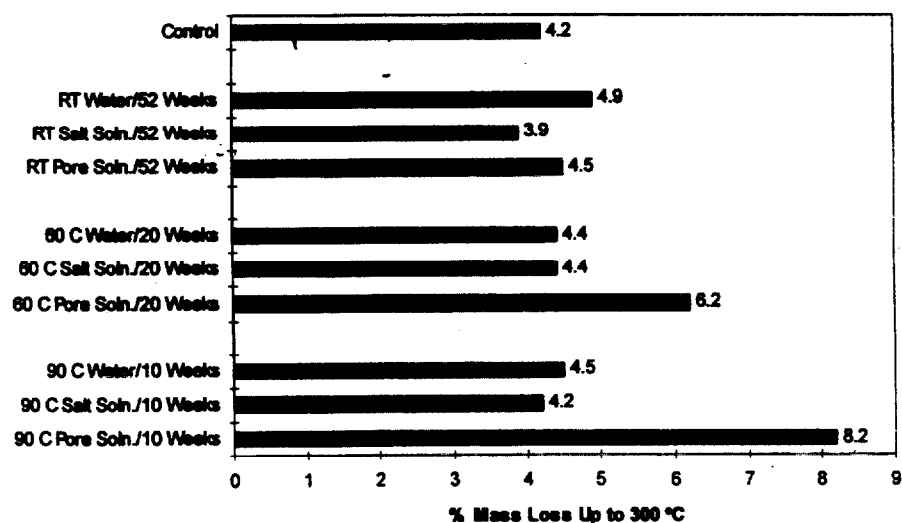


(c)

Figure 2: Isopolyester glass transition temperatures determined by DMTA following exposure to water, salt solution and concrete pore solution at (a) ambient temperature, (b) 60 °C, and (c) 90 °C (estimated standard deviation is ± 2 °C).

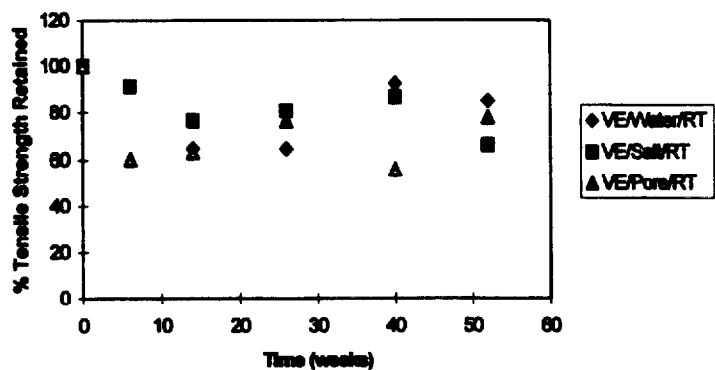


(a)

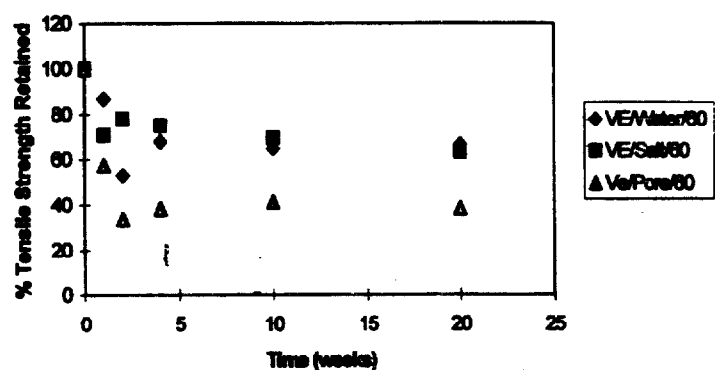


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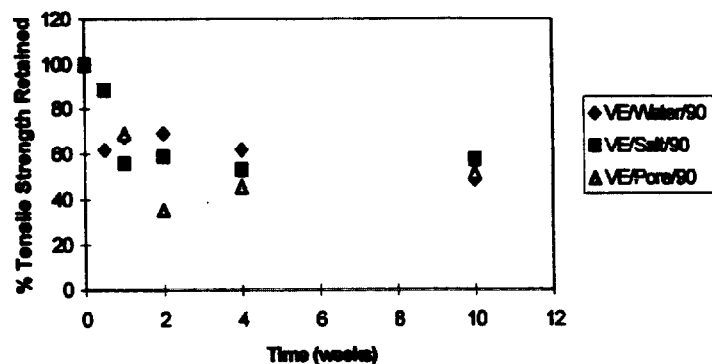
Figure 3: Percent mass loss measured by thermogravimetric analysis between ambient temperature and 300 °C for (a) vinyl ester and (b) isopolyester (estimated standard deviation is $\pm 0.5\%$).



(a)

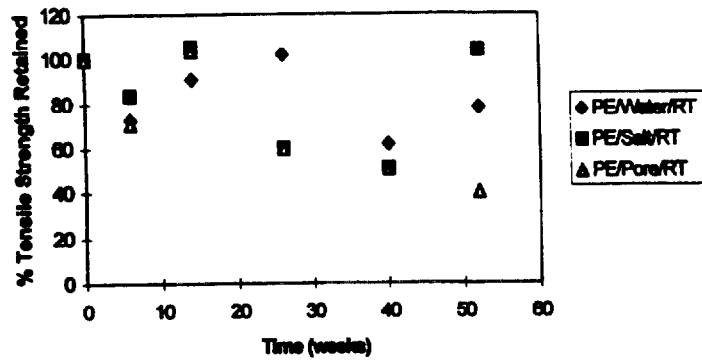


(b)

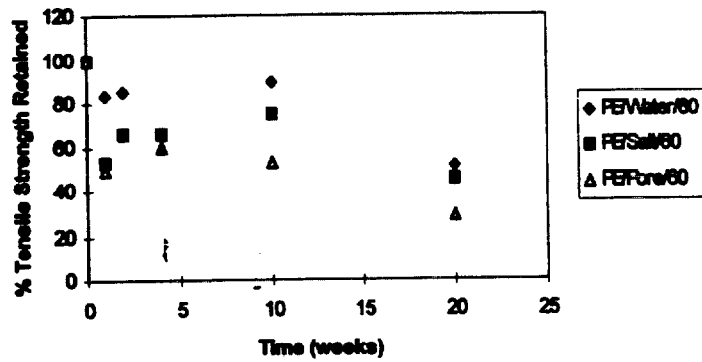


(c)

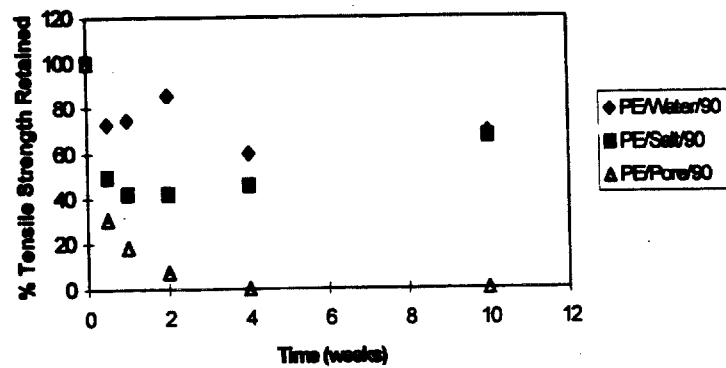
Figure 4: Percentage of vinyl ester tensile strength retained following exposure to water, salt solution and concrete pore solution at (a) ambient temperature, (b) 60 °C, and (c) 90 °C (standard deviation of the data is estimated to be $\pm 23\%$).



(a)



(b)



(c)

Figure 5: Percentage of isopolyester tensile strength retained following exposure to water, salt solution and concrete pore solution at (a) ambient temperature, (b) 60 °C, and (c) 90 °C (standard deviation of the data is estimated to be $\pm 23\%$).

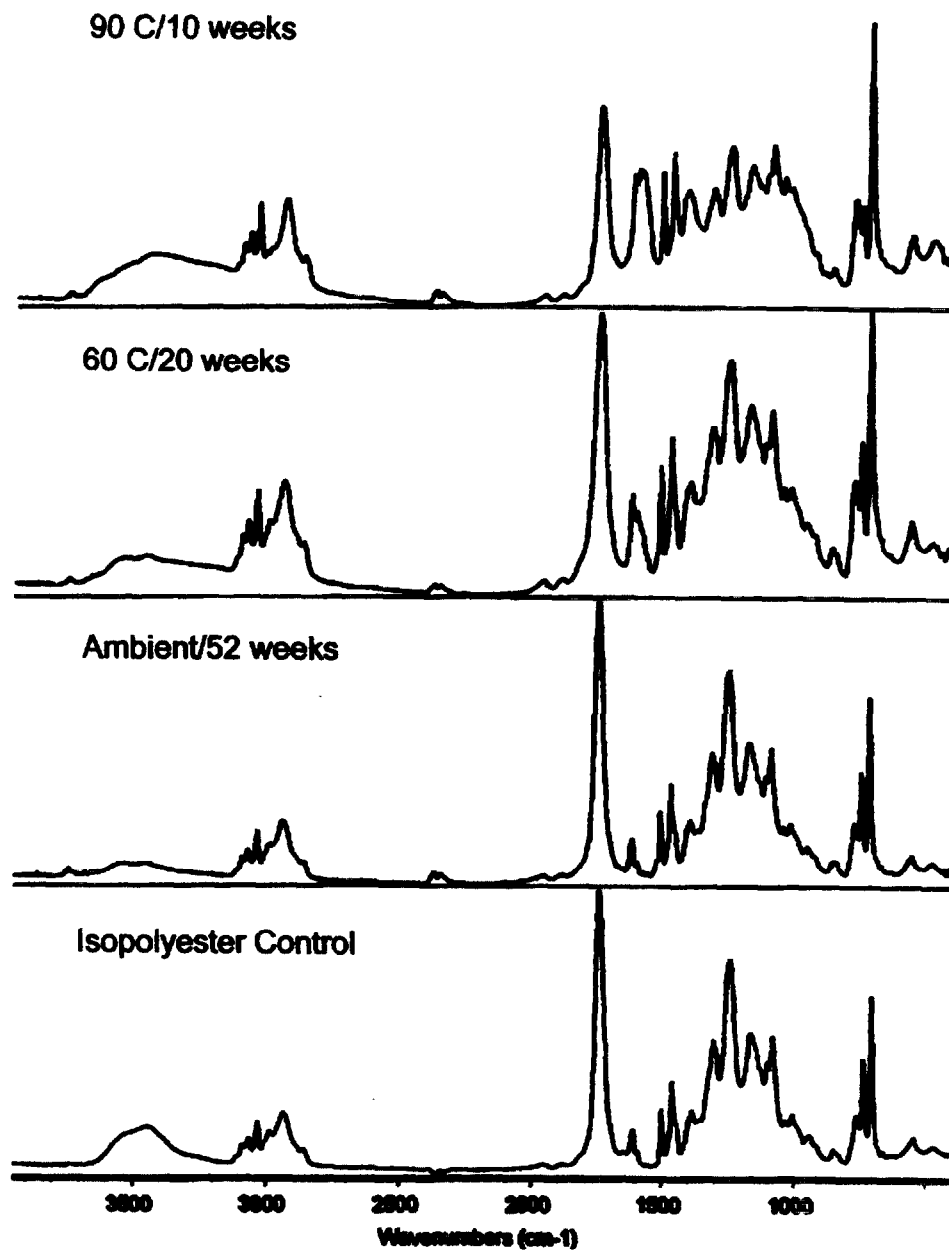


Figure 6: Infrared spectrum of isopolyester before and after exposure to concrete pore solution at ambient temperature, 60 °C and 90 °C.